Organo-erbium systems for optical amplification at telecommunications wavelengths.

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Abstract

Modern telecommunications rely on the transmission and manipulation of optical signals. Optical amplification plays a vital part in this technology, as all components in a real telecommunications system produce some loss. The two main issues with currently used amplifiers, which rely on erbium ions in a glass matrix, are the difficulty in integration onto a single substrate and the need of high pump power densities to produce gain. Here we show a potential organic optical amplifier material which demonstrates population inversion when pumped from above using low power visible light. This system is integrated into an organic light emitting diode (OLED) demonstrating that electrical pumping can be achieved. This opens the possibility of direct electrically driven optical amplifiers and optical circuits. Our results provide an alternative approach to producing low cost integrated optics that is compatible with existing silicon photonics and a different route to an effective integrated optics technology.

Modern telecommunications networks are based around a worldwide back-bone of fibre-optic cables which encircle the globe carrying data at the speed of light. Despite the phenomenally low losses experienced in these fibres it is still necessary to regularly amplify the optical signals and this is traditionally performed using erbium doped fibre amplifiers (EDFAs) [1]. These rely on an intra-atomic transition in the erbium ion that emits at a wavelength of 1.5 μm, the low loss window of silica fibres. Due to the low absorption coefficient of erbium ions, a separate pump laser must be launched axially down erbium doped fibres of 10-30 m length to achieve population inversion and thus optical gain. The properties of erbium-based amplifiers can, in principle, be enhanced by incorporating erbium ions into organic hosts [2,3,4] containing chromophores (light harvesting chemical groups providing strong absorption in the organic) that couple to the erbium (a phenomenon called sensitization), which allows for pumping with lower intensity sources, such as light emitting diodes (LEDs) and amplification in much shorter lengths. Attempts to implement this idea have been hampered by the quenching of the infra-red emission of erbium ions by C-H or O-H oscillators present in most organics [5-8] which result in poor efficiencies and photoluminescence lifetimes orders of magnitude smaller than required. Here we show how amplification can be obtained by a new material system that combines the long fluorescence lifetime of a fluorinated organic erbium complex with a fully fluorinated chromophore to produce a medium with exceptional sensitization ($>10^4$ relative to direct absorption) plus an internal quantum efficiency of ~7%. This system has been implemented into planar amplifying waveguides to demonstrate the onset of optical gain at the 1.5 μm telecommunication window [2,9]. This approach allows for the development of a variety of structures which can then be integrated onto any flat substrate; for example, integration onto silicon would allow for optical functionality to be added to silicon devices [10] with the additional advantage of pumping from above which simplifies device design. For example,

optical splitters are commonly fabricated on silicon substrates but a 32 way splitter produces a loss of at least 15 dB per channel which therefore requires optical amplification (or very high launch powers). Using the structures outlined in this work we could design a splitter where gain is provided throughout the device or with a small integrated optical amplifier after the splitter resulting in a loss-free device. Due to the favourable properties of the employed organic semiconductors, this system has been integrated into an organic light emitting diode (OLED) demonstrating that electrical pumping of this medium can be achieved which opens the possibility of a direct electrically driven optical amplifiers and opto-electronic circuits. The goal of producing efficiently sensitized erbium in a material that can be used for wave-guiding has been the subject of much research for ~20 years. Many researchers have focused on the use of either nanocrystalline silicon particles in an erbium doped silicon dioxide matrix or organic erbium complexes to achieve this. Nanocrystalline silicon sensitization has received a remarkable degree of attention [11] and yet there have been very few demonstrations of optical gain and these have all required very high optical pump powers [12]. Indeed, work has suggested that net gain in this system may be impossible with continuous wave excitation due to intrinsic carrier absorption and the low coupling between the silicon nanocrystals and the erbium ions distributed in the wave-guide [13]. Similarly, despite over 10 years of work on organic erbium complexes there has hitherto been remarkably little progress in making systems with sufficiently promising properties to be considered for use in optical amplifiers or lasers. Although some organic chromophores have been proved to sensitize the erbium in suitable spectral ranges and, some deuterated [5,6,8] and halogenated complexes [14,15,16] show a considerable enhancement of the erbium emission properties and provide relatively long lifetimes, the reality is that both conditions are never fulfilled to an operational extent. One of the problems with producing perfluorinated ligands and chromophores is that the strongly electron withdrawing properties

of the fluorine atoms makes it difficult for the ligands to bind with lanthanide ions and many of the compounds are not chemically or thermally stable. Apart from the synthesis-related problems, this fact represents an extra difficulty towards processing the materials via conventional organic vapour deposition techniques, which is essential to achieve the purity and optical quality required for waveguide applications.

These problems have been overcome by separating the chromophore function from that of producing a high efficiency organic environment for the erbium ion (strong, long lived 1.5 μm emission) while creating a highly efficient energy transfer between the chromophore and the erbium [17,18] in a composite material. With this strategy the optical quality is exceptional, the refractive index is kept uniform within the waveguide, the erbium ions are uniformly distributed and all are in intimate contact with light harvesting chromophore molecules. Thus, this new material system is based on an erbium complex that does not demonstrate sensitization in the visible region, erbium(III) tetrakis(pentafluorophenyl)imidodiphosphinate, $Er(F\text{-}TPIP)_3$ [14], but which provides a long luminescence lifetime for the encapsulated erbium ions, co-evaporated with a perfluorinated zinc-based organic chromophore, the zinc(II) salt of 2-(3,4,5,6-tetrafluoro-2-hydroxyphenyl)-4,5,6,7-tetrafluorobenzothiazole, $Zn(F\text{-}BTZ)_2$ [19]. This choice of materials is fully vacuum compatible and high quality films can be grown onto any substrate. We have used this approach to grow a waveguide, on to thermally grown silicon dioxide layer on a silicon substrate. This waveguide demonstrated population inversion in the erbium ions, while being optically pumped normal to the surface at very low power (~3 mW) at a wavelength of 405 nm. We have gone on to demonstrate that this system can be fully integrated into OLED structures producing the possibility of an electrically pumped optical amplifier. Our technology opens the possibility of producing organic optical amplifiers and circuits operating at the key telecommunications wavelength of 1.5 μm.

The absorption spectrum for a 100 μm crystal of $Er(F\text{-}TPIP)_3$ is presented in figure 1A; it can be seen that there is clear absorption directly into the Er^{3+} ions but no evidence of ligand absorption at wavelengths greater than 350 nm. In contrast figure 1B shows the excitation spectrum, recorded at the Er^{3+} emission peak, for a 250 nm thick film of $Zn(F\text{-}BTZ)_2$, co-evaporated with 30% $Er(F\text{-}TPIP)_3$. In this doped film there is no evidence of direct excitation into the Er^{3+} ions, and the excitation is dominated by a broad band which extends from the UV at <350 nm to ~475 nm in the blue. This is unlike the excitation spectra of other erbium-containing organic materials [15] which provide only modest (factor of ~5) sensitization. This excitation spectrum matches perfectly to the emission from commercially available and highly efficient high-power blue LEDs.

As the excitation spectrum shows no evidence of direct absorption into the erbium ions (any absorption that must be present is below the sensitivity limit) we are only able to give a minimum value for the enhancement of sensitization provided by the $Zn(F\text{-}BTZ)_2$ complex. The ratio of the size of the integrated area under the excitation spectrum from 350 nm to 500 nm to that measured in the region from 510 nm to 540 nm, which includes the strong 520 nm $^4I_{15/2} \rightarrow {}^2H_{11/2}$ transition, gives a *minimum* sensitization for the doped film in the order of 10^4, relative to direct absorption into the Er^{3+} ion. In order to demonstrate that this sensitization is directly attributable to the $Zn(F\text{-}BTZ)_2$ complex we show in figure 1B the absorption spectrum from a 250 nm thick layer of pure $Zn(F\text{-}BTZ)_2$. This absorption spectrum has a band that is coincident with that for the excitation spectrum of the doped layer, proving unambiguously that it is the Zn complex that sensitizes the erbium emission. The infrared photoluminescence spectrum of the doped $Zn(F\text{-}BTZ)_2$ film when excited at a wavelength of 405 nm is shown in figure 1C. The emission spectrum shows strong luminescence from the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.

Crucial information on the nature of the sensitization and energy transfer processes can be gained from time resolved measurements. Time resolved photoluminescence measurements at the peak of the erbium emission (Figure 2A) recorded using 5 ns pulses at a wavelength of 417nm (near the peak of the excitation spectrum and away from any direct Er^{3+} ion absorption) show a rise time of ~0.5±0.05 μs followed by a decay which has at least two components with an average lifetime of ~0.86±0.08 ms (the lifetime of the pure $Er(F\text{-}TPIP)_3$ is 200μs). The intrinsic radiative lifetime of Er^{3+} ions, as derived from the corresponding $^4I_{15/2} \rightarrow {}^4I_{13//2}$ absorption spectrum using a single crystal of $Er(F\text{-}TPIP)_3$, is 13±1 ms [20] for this transition indicating a quantum efficiency of ~7% [Supplementary Figure S1], the highest ever reported for erbium in an organic complex. Such high photoluminescence efficiency, coupled with the high sensitization, is critical for population inversion and thus gain.

We describe the observed energy transfer processes from an organic chromophore into the Er^{3+} ion in figure 2B [2]. Absorption of a photon in the organic moiety generates singlet excitons, S_1. It is understood [21] that a change in spin number is required to transfer the excitation from the organic S_1 state to the Er^{3+} multiplets and that a prior change from the singlet into a lower lying triplet state, T_1 (inter-system crossing) allows this coupling to occur more efficiently. In this system the effect of the eight fluorine atoms on each benzothiazole ligand favours the spin mixing and intersystem crossing, through the enhanced spin-orbit interaction caused by the higher *Z* of fluorine compared to hydrogen, and hence contributes to efficiently transferring the energy to the lanthanide ion multiplets directly and via the intermediate state T_1 [22].

The time evolution of the erbium infrared emission when excited using square modulation of length 4 ms from a 405 nm laser, which again is only absorbed by the $Zn(F\text{-}BTZ)_2$ chromophore, can be seen in figure 2B. Compared with the excitation using the 5 ns pulsed

laser, this quasi-continuous wave (CW) measurement gives a greatly increased rise time of 0.8±0.08 ms. This different behaviour can be explained if we consider that for the transient measurement (5 ns pulse) there is no time to build up a significant excitation population and it is expected that the primary energy transfer into the Er^{3+} ions will be through the short lived (<100 ns) singlet state in the $Zn(F\text{-}BTZ)_2$. The 0.5 μs rise time is therefore mainly contributed by the conversion of initially populated levels in the Er^{3+} ions (green arrow in the diagram in figure 2) into the emissive $^4I_{13/2}$ state. However, for the long excitation time the population in the triplet state of the $Zn(F\text{-}BTZ)_2$ increases with continuing excitation due to the long lifetime of the triplet state under optical excitation (~270 μs) [Supplementary Figures S2 and S3]. These triplets can then transfer their energy into the Er^{3+} ions (red arrows in the diagram in figure 2) and the rise time of the erbium emission is primarily determined by the lifetime of that state. Importantly, long lived triplets can diffuse in the composite material and reach relatively distant Er^{3+} ions, which permit that relatively low excitation powers densities can build a significant population of excited erbium ions compared to having the sensitizer bound to the ion [23]. The sensitization and luminescence properties of the $Zn(F\text{-}BTZ)_2$ – $Er(F\text{-}TPIP)_3$ system make it an ideal candidate for use as an optical amplifier operating at telecommunications wavelengths.

Given the interesting properties of this system we fabricated an 8 mm long waveguide formed from a 2 μm evaporated film of $Zn(F\text{-}BTZ)_2$ doped with 30% $Er(F\text{-}TPIP)_3$ (the concentration of erbium ions in the waveguide is ~1.8×10^{20} cm^{-3}) on to a 700 nm thermally grown silicon dioxide layer on a silicon substrate. This waveguide supports four modes with 96% of the guided light propagating in the organic core (Supplementary Figure S4 and Table S1). Figure 3 shows the intensity of the 1.5 μm luminescence (modulated at 190 Hz) observed from the edge of the waveguide, with and without an optical pump. It can be clearly seen that the intensity of the modulated probe signal is amplified by ~85% when the pump laser is

switched on. This equates to an apparent gain of 3.3 dB/cm. Given that the main loss mechanism in the waveguide is self-absorption due to the erbium ions in the ground state we can calculate the loss due to self-absorption in the waveguide to be -6 dB/cm (Supplementary Figure S5). Pumping erbium ions into the $^4I_{15/2}$ excited state removes this absorption and can also provide gain through stimulated emission. Therefore by reducing the self-absorption by just over a factor of two we have managed to bring the system to the edge of population inversion. This assumes that the excited erbium ions are distributed uniformly throughout the 2μm thick layer. In reality the penetration depth of the 405 nm pump (which is at the peak of the absorption curve of the composite material) is only ~0.5μm, which implies that the lower 75% of the waveguide layer has negligable excited erbium ions and hence will be nearly fully absorbing. Therefore we expect that there should be significant population inversion and real positive gain in the top part of the waveguide which is absorbing the pump light.

While the optically pumped system we have demonstrated could be widely utilised for optical gain as it is compatible with cheap, highly efficient, high-power LEDs, the applications of this system would be more far-reaching if the erbium ions were excited electrically. We have therefore demonstrated that $Er(F\text{-}TPIP)_3$ doped $Zn(F\text{-}BTZ)_2$ can indeed be used to produce IR OLEDs. Figure 4 shows the electroluminescence spectrum from a layer of pure $Zn(F\text{-}BTZ)_2$. Two peaks are clearly visible. The higher energy peak is due to the singlet state and has a short lifetime (<100 ns). The lower energy peak is due to the triplet state and has two lifetime components, a major one at ~ 50 μs and a smaller component at ~5 μs. These are somewhat lower than the 270 μs we have measured in a pulsed photoluminescence experiment and can probably be attributed to quenching of the triplets in the OLED. One possible mechanism that is known to occur is triplet-polaron quenching [24,25], although there may be other mechanisms present such as triplet-triplet annihilation [25] due to the much higher triplet population present in the OLED. Figure 4 also shows the infrared electroluminescence from

an OLED where the $Zn(F\text{-}BTZ)_2$ was doped with 20% of $Er(F\text{-}TPIP)_3$ which demonstrates that efficient electrical pumping of this system is possible. In this doped OLED the visible emission is solely due to the singlet emission. This is dramatic evidence for highly efficient energy transfer between the triplet state and the erbium ions in the $Er(F\text{-}TPIP)_3$. The efficiency of triplet mediated energy transfer as a mechanism for exciting erbium ions in this composite system opens novel possibilities for still further improving the sensitization. Whilst the presence of fluorine and Zn contributes to increasing the population of triplets upon optical excitation of the chromophore, heavier halogens or central metals can be expected to increase the number or triplets and thus the overall sensitization of erbium ions. An alternative approach would be to utilise halogenated versions of the heavy metal complexes used as triplet emitters in OLEDs.

In summary, we have demonstrated a potential new gain medium based on a new organic semiconductor system showing high efficiency, sensitized infra-red luminescence from erbium ions that is based on the separation of the absorption and emission functions into separate compounds which have efficient energy transfer between them. This allows for much greater control over the individual functions which gives us fine control over the properties through design at a molecular scale. The approach is fully compatible with vacuum processing and devices can be deposited onto any substrate. A simple planar waveguide on silicon demonstrated both optical confinement and the onset of population inversion in the erbium ions, using a pump normal to the surface with an intensity of only ~3 mW. Moreover, this same active layer has been demonstrated to operate in electroluminescence mode using an OLED structure yielding significant emission from erbium. This work opens exciting possibilities for new hybrid integrated optoelectronic devices and applications such as organic optical amplifiers and lasers to be easily integrated into other materials systems.

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Supplementary information is linked to the online version of the paper at www.nature.com/nature

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Author Contribution HY prepared samples, collected data and modeled the waveguides. ZL, YP, YZ, YX, CW and TL synthesized and characterized the materials. HY, AS and GA helped with the waveguide fabrication. ZL produced and characterized the OLEDs. PBW directed the chemical synthesis program. IH contributed to the strategy and directed the

experiments. WPG designed the study and wrote the paper. All authors discussed the results and commented on the manuscript.

Author Information The authors declare no competing financial interests

Figure Captions

Figure 1

Optical spectra of organo-erbium materials. (**a**) The absorption spectrum for a single crystal of $Er(F\text{-}TPIP)_3$ showing characteristic absorption into the Er^{3+} transitions (all the transitions shown are from the $^4I_{15/2}$ ground state and labelled according to the excited state, using standard nomenclature). Note that there is no ligand absorption in the visible region of the spectra. (**b**) The excitation spectrum of the doped film recorded at the erbium emission peak (black solid line). Direct excitation into the erbium ions was too weak to be recorded in this experiment. The blue dotted line is the absorption spectrum for a film of the chromophore $Zn(F\text{-}BTZ)_2$. The dashed green line is the photoluminescence spectrum for $Zn(F\text{-}BTZ)_2$ powder. (**c**) The infrared photoluminescence $^4I_{13/2} \rightarrow {}^4I_{15/2}$ from the erbium atoms in the doped film excited at a wavelength of 405 nm.

Figure 2

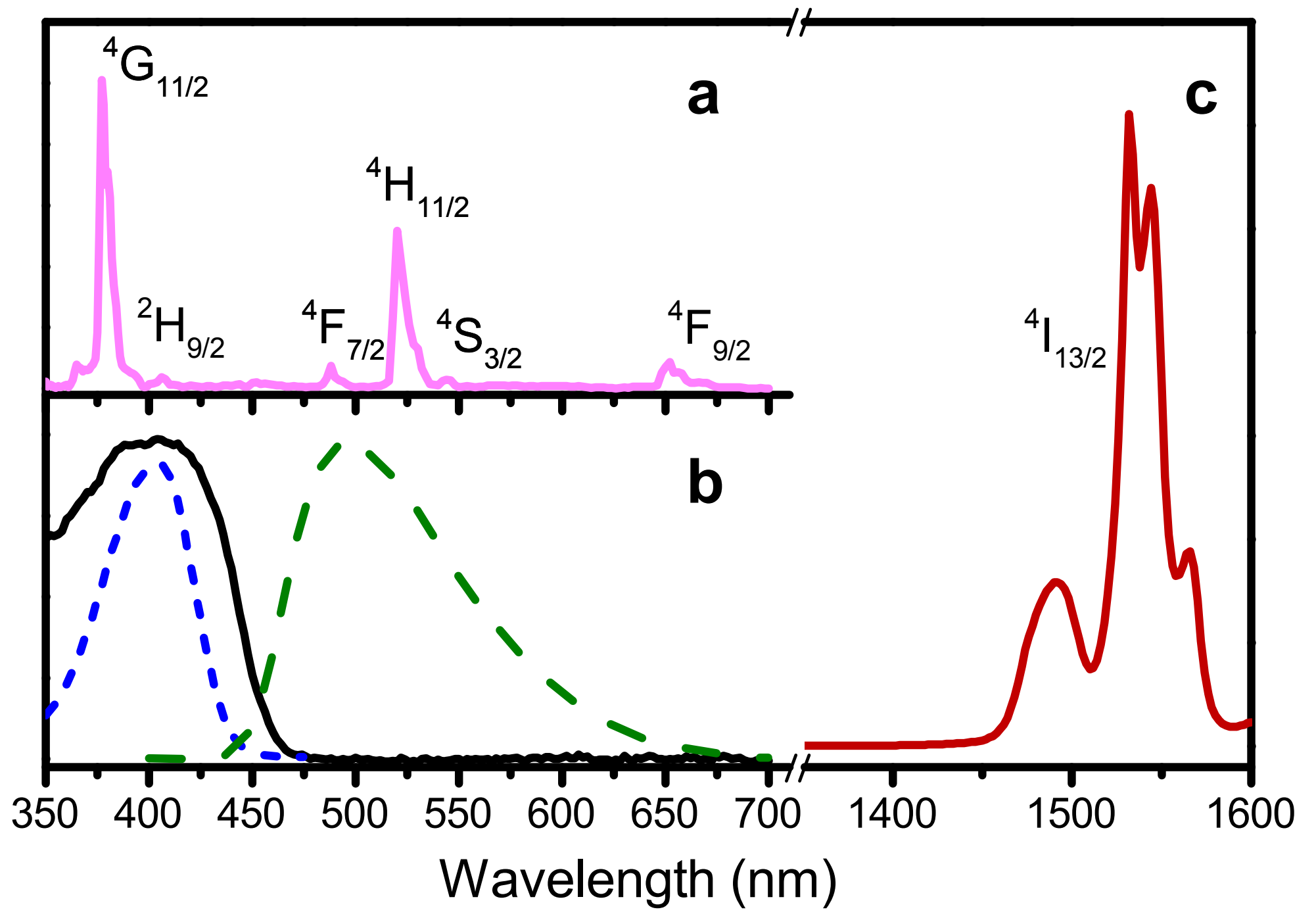
Time dependence of erbium $^4I_{13/2} \rightarrow {}^4I_{15/2}$ photoluminescence from the doped film. (**a**) Excited using a 5 ns pulse at 417 nm excitation and (**b**) excited using a square 4 ms pulse at 405 nm. The long rise time is due to the build-up in the $^4I_{13/2}$ level due to the long lifetime of the transition to the ground state. Also shown is the Jablonski diagram for the system highlighting the energy transfer from both the singlet and triplet states in the $Zn(F\text{-}BTZ)_2$. Dashed arrows represent non-radiative decay.

Figure 3

Schematics of the waveguide structure used for gain measurements. A probe laser was used to excite photoluminescence in the waveguide which was measured at the opposite edge. The graph shows the intensity of the signal with and without a pump laser. The presence of the pump laser amplifies the signal intensity by 85%.

Figure 4

Normalised electroluminescence from doped and undoped OLEDs. Two peaks are observed from the undoped device: singlet emission at ~500 nm and triplet emission at ~610 nm. In the device where the $Zn(F\text{-}BTZ)_2$ is doped with 20% $Er(F\text{-}TPIP)_3$ the triplet emission of $Zn(F\text{-}BTZ)_2$ can no longer be seen and there is strong infrared luminescence from the erbium $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition.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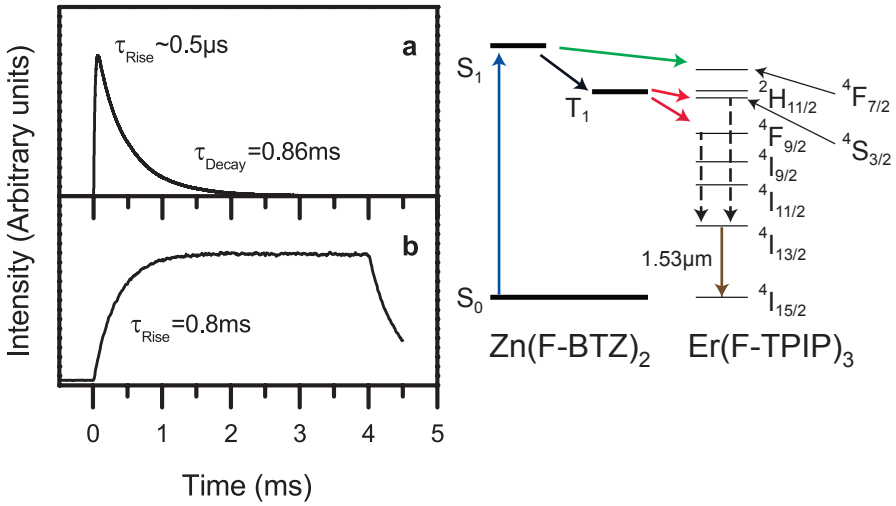
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τDecay=0.86ms
b
τRise=0.8ms
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1
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Time (ms)
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T1
S0
2H11/2
4F7/2
4S3/2
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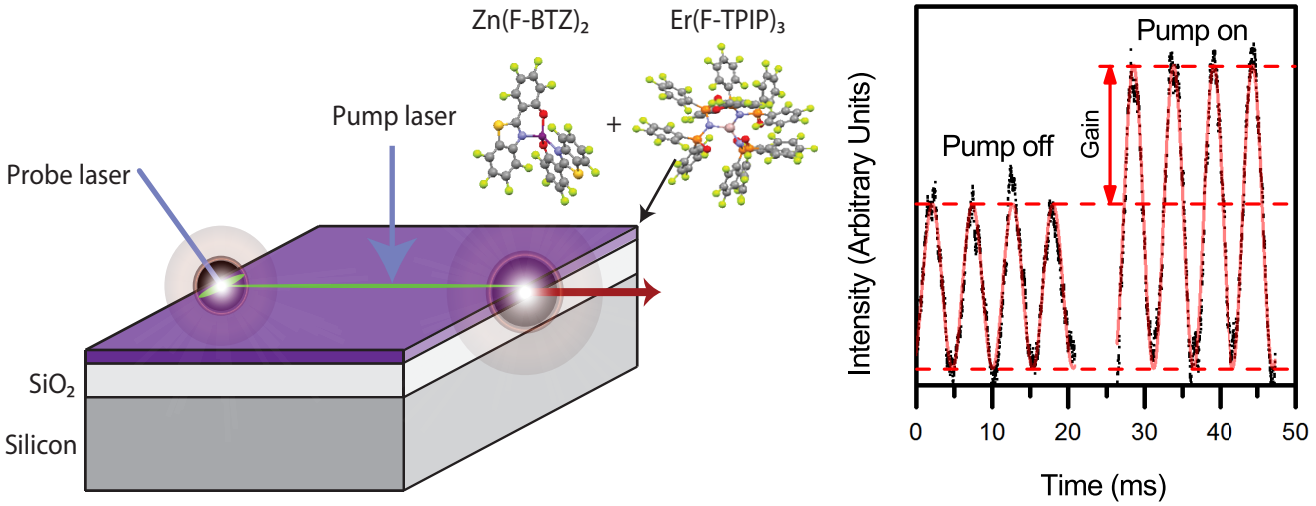
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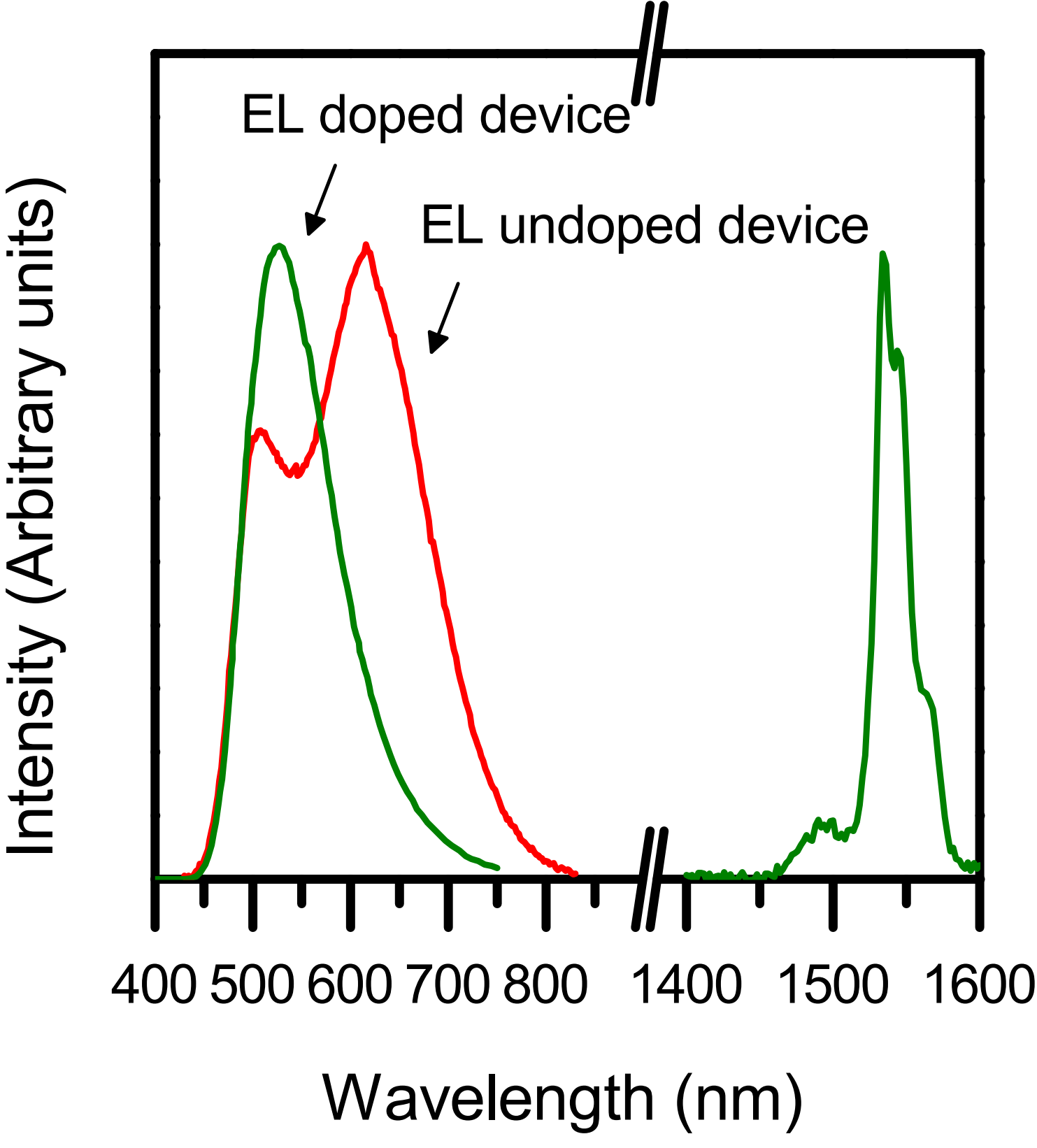
EL doped device
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